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研究課題名(和文) Stabilization of hazardous heavy metals in municipal solid waste incineration (MSWI) fly ash using natural fishbone hydroxyapatite (HAP): A novel approach to the treatment of waste material

研究課題名(英文) Stabilization of hazardous heavy metals in municipal solid waste incineration (MSWI) fly ash using natural fishbone hydroxyapatite (HAP): A novel approach to the treatment of waste material

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研究成果の概要(和文)：日本の3つの焼却施設からのMSWIフライアッシュの詳細な特性評価を行い、いくつかの魚の骨種とそのハイドロキシアパタイト含有量が分析されました。バッチ実験とカラム実験は、さまざまな分析条件で実施しました。フライアッシュから重金属を浸出することにより、シミュレートされた浸出液が生成されました。重金属(PbとZn)はフライアッシュで安定化されました。3つの安定剤の使用について逐次分析を行いました。中国、トルコ、チュニジアで開催された3つの会議で発表されました。Waste Management に記事が1件掲載されました。もう1冊の原稿が審査中です。

研究成果の学術的意義や社会的意義

この研究は、フィッシュボーンがFAの重金属、特にPbとZnを安定化できることを示しました。この手法では、10%の廃棄フィッシュボーンをFAに追加することにより、28日間の沈降期間後に86%以上の鉛を安定化できました。Znの安定化は、より長い沈降期間(28日)で効率的でした。この技術は、廃棄魚の骨の処理量を減らし、リサイクルを促進するのにも役立ちます。さらに、フィッシュボーンとFAの最終的な混合量は、セメント化FAの量よりも少なくなる可能性があります。したがって、この手法は、比較的低コストで環境に優しく、持続可能な手法として期待されています。

研究成果の概要(英文)：In this research, we completed the following: A detailed characterization of MSWI fly ash from three incineration plants in Japan was performed. Several fishbone species and their hydroxyapatite contents were analyzed in detail. We conducted new sets of batch and column experiments under different analytical conditions to evaluate the effects of fishbone species on the leachability of heavy metals in fly ash. We generated Simulated leachates by leaching heavy metals from fly ash and stabilizing them using fish bone hydroxyapatite. Heavy metals were successfully stabilized in fly ash in the order of 80 to 100% for Pb and Zn. We also performed the sequential analysis on the use of three stabilizing agents (zeolite, fishbone, and rice husk ash). The achievements were presented in three international conferences in China, Turkey, and Tunisia, two of them received best paper awards. One article was published at Waste Management journal (August 2022), and one more article is under review.

研究分野：Environmental Engineering

キーワード：Municipal Solid Waste Fishbone-Hydroxyapatite Apatite IITM Heavy metals Stabilization Phosphate Fly ash Incineration

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1 . 研究開始当初の背景

Incineration or waste to energy (WtE) technology is a commonly used method worldwide for treating municipal solid waste (MSW). Incineration reduces the weight and volume of waste by about 70% and 90%, respectively. In Japan, the share of solid waste incineration was up to 75% in 2013. Although incineration is efficient for MSW treatment, one of the shortcomings of this technology is producing significantly large amounts of solid residue (e.g., **fly ash**). Due to the high content of heavy metals (Pb, Zn, Cu, Cd, Cr, Sb, etc.), chlorine, organic compounds, soluble salts, and the fineness of its particles, the resulting **fly ash (FA)** is classified as a hazardous waste. FA requires special treatments to prevent environmental risks before utilization or landfilling. FA can be treated in several ways, including solidification with cement or geopolymer, chemical stabilization using additives (i.e., chelate compounds), advanced separation, thermal treatment via melting, synthetic phosphate (such as phosphoric acid) treatment, and hydrothermal techniques. **Soluble phosphate** has been widely used as a means of chemical treatment to convert heavy metals into insoluble compounds. **Soluble phosphates** react with *multivalent cations* to form **insoluble orthophosphates**. The final product of the reaction of soluble phosphate with metal ions is an insoluble metal phosphate that resembles a naturally occurring mineral and is stable in geological environments. One of the typical examples of lead phosphate with very low solubility in a wide pH range is hydrargyrite, $Pb_5(PO_4)_3Cl$. Another frequently used substance is the apatite family, with **hydroxyapatite (HAP)**, which forms the lead member $[Ca_5(PO_4)_3(OH)]$ of a large class of substituted compounds of similar compositions.

Fishbones and the skeleton of mammals are composed of **calcium phosphate**, highly resembling HAP. HAP from bones, bone char, and synthetic HAP has been investigated for their absorption capacity from aqueous solutions for retaining heavy metals. HA can effectively be used for the treatment of heavy metal polluted waste materials. Biogenic apatite (in fishbone) is comparable to other phosphate sources and found to be initially less contaminated with heavy metals. It is more soluble, enhancing metal sequestration and providing a slow release of phosphate in the long run. Many studies have been performed on the efficiency of phosphates and particularly apatites $[M_{10}(PO_4)_6(OH)_2, M: \text{Metal}]$, and the mechanisms involved, in removing and immobilizing heavy metals from wastewater, groundwater, dredged sludge, and contaminated soil.

2 . 研究の目的

The primary objectives of this study was as follows: (1) To evaluate the feasibility of using waste **fishbone hydroxyapatite (FB-HAP)** and its roles in stabilizing heavy metals in FA, (2) To enhance the efficiency of FB-HAP by improving different parameters without thermal treatment (i.e., modification of fishbone processing, using bones from different fish species, longer contact time, lower dosage of fishbone, FB-HAP size fractionation, and the state of the admixture defined by water/solid ratios), and (3) To provide evidence to elucidate the mechanism of the reactions occurring between FB-HAP and heavy metals in IFA. Similar experiments have been performed using a commercially available fishbone product (Apatite IITM) to compare its efficiency with FB-HAP (a product developed for the current research). In this study, the effect of fishbone particle size was studied to evaluate the extent of lead (Pb) stabilization in MSWI fly ash. Based on this proposal, there was very strong passion to investigate whether non-toxic fishbone apatite could be an effective alternative for the stabilization of divalent heavy metal ions with emphasis on fly ash from waste incineration. As an alternative to landfilling, most of the phosphate-treated ash is expected to be safe for utilization as mineral filler in value added products such as road base or cement blocks.

3 . 研究の方法

1) *Collection and preparation of fishbone*

Waste fishbone was collected from several fish markets in Fukuoka City, Japan. The collected bones belonged to various fish species, including yellowtail, sea bream, salmon, mackerel, horse mackerel, lizardfish, fly fish, and Japanese amberjack or yellowtail. The bones collected were associated with plenty of flesh and soft tissues. Therefore, compared to a previous study, a different approach was adopted to efficiently remove fatty substances (lipid) from the collected bones and minimize the potential impact of such substances on metal stabilization.

2) *MSWI fly ash collection*

Approximately, 50 kg of FA material was collected from a WtE facility in Kyushu, Japan. Another 20 kg of FA material was collected from a WtE facility in Hokkaido, Japan. FA material was collected from both facilities prior to chelate stabilization. Materials were stored in hermetically sealed containers after collection. Both materials were used in the experiments without any pretreatment. IFA materials were manually ground in an agate mortar for bulk mineralogical and compositional analyses and leaching experiments.

3) *Fly ash and fishbone characterization*

The bulk chemical composition of FA was determined using X-ray fluorescence (XRF) technique. Elemental concentrations in the leachate were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES). Mineral phases of both FA and fishbone were determined using X-ray diffractometry (XRD). Particle analysis of both IFA and fishbone, before and after experiments, was performed using a scanning electron microscope combined with an energy dispersive X-ray (SEM-EDX) detector in backscattered electron (BSE) mode.

4) *Experimental conditions*

Two different experimental conditions were designed to investigate the effects of FB-HAP and Apatite IITM on heavy metals immobilization in FA. Tests were performed at room temperature in 250 mL polypropylene bottles. In each bottle, 20.0 g of fly ash (from sources S and K) was mixed with 2.0 g of FB-HAP or Apatite IITM (fishbone dose of 10%), and the water-to-solid ratios (W/S) were adjusted to 1.0 and 1.5 mL/g. Ultrapure water was used as the test solution in all experimental conditions. The bottles were settled at ambient conditions for 6, 12, 24 and 672 h (28 days) for the FA sample from source S. The FA sample from source K was settled only for 24 h at a W/S ratio of 1.5 mL/g. After each settlement period, ultrapure water was added to each bottle in order to increase the total leachant to 200 mL. The admixtures were subjected to the standard Japanese leaching test (JLT-46). After the leaching test, each bottle was centrifuged at 3000 rpm for 20 min, and the solid and liquid phases were separated using a 0.45 μ m pore-size membrane filter. Each test was run in duplicate and the results were calculated as mean values with standard deviation.

4 . 研究成果

1) *Effects of FB-HAP and Apatite IITM on the stabilization of Pb and Zn*

The effects of both FB-HAP and Apatite IITM on Pb and Zn stabilization in FA were investigated at two different mixing ratios and different settling times. The effectiveness of both fishbone products was evaluated by metal removal efficiency in the leachate after conducting the JLT-46 test. The concentrations of Pb and Zn in the leachate were identified by ICP and the stabilization efficiency of the target metal was calculated using the following Equation:

$$M_R(\%) = 1 - \frac{C_t}{C_c} \times 100$$

M_R is the target metal removal efficiency (%), C_t is the metal concentration in test group, and C_c is the metal concentration in the control group.

The results in Table 1 shows that both FB-HAP and Apatite IITM completely stabilized Pb and Zn in the FA sample from source K within a 24 h settling time due to low initial concentrations of both metals (3.85 mg/L and 0.5 mg/L, respectively). This prominent result suggests that FB-HAP can be used directly as an effective metal stabilizer in incinerators with low levels of heavy metals in their fly ash products. At relatively higher levels of Pb (48.5 mg/l in IFA sample from source S), 100% stabilization could not be achieved.

Table 1. Concentration of Pb and Zn in the leachates of fly ash sample K at the presence of FB-HAP and Apatite IITM under 1.5 W/S at 24 h contact time

FA sample	Fish bone	W/S (mL/g)	Pb (mg/l)	Zn (mg/l)	Efficiency (%)
K	FB-HAP	1.5	0.0	0.0	100
	Apatite II TM				
Ctrl*			3.85	0.5	

*Ctrl. (control group): Concentration in the leachate of IFA (without fishbone) after 6 h-leaching process.

As shown in Fig. 1, a significant amount of Pb eluted from FA sample (from source S) was immobilized by FB-HAP within the first few hours. FB-HAP was able to stabilize Pb in fly ash, and the stabilization gradually improved over time. Pb removal efficiency reached 77.49% after 6 h of settling time at the FB-HAP dose of 10%. Although short-term settling can stabilize a significant amount of Pb in fly ash, a comparatively longer period (28 days) can enhance Pb stabilization (up to 86.18%) at W/S-1.5 mL/g. This implies that, at longer contact time, a different and more efficient mechanism promotes the heavy metal stabilization process by natural waste FB-HAP.

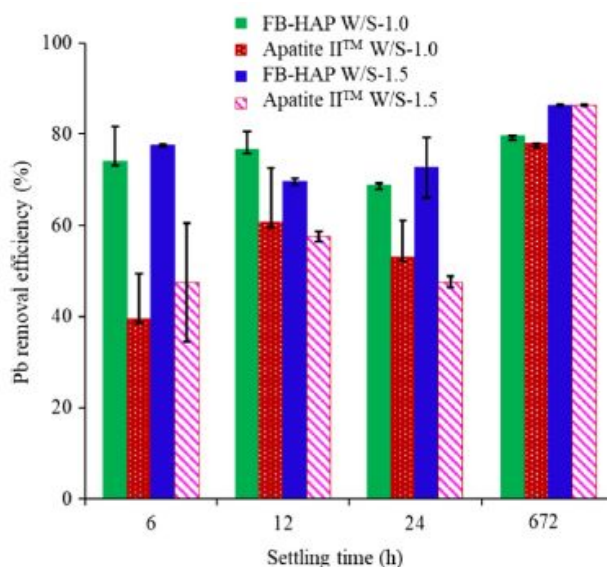
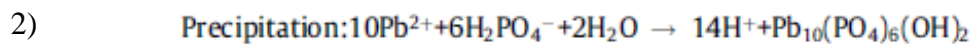
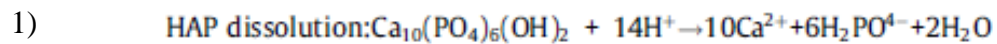


Fig. 1. Pb removal efficiency with FB-HAP and Apatite IITM.

2) Mechanisms of heavy metal stabilization by hydroxyapatite

Regarding HAP as a scavenger of toxic ions, multiple mechanisms are expected to be involved in the HAP-metal retention process. In this regard, two mechanisms have been proposed to explain the retention of metals by HAP from the solution. First, at the water/HAP interface, ions are easily adsorbed, leading to the second mechanism of dissolution-precipitation or ion-exchange reactions and/or complexation. Based on this assumption, the dissolution-precipitation and ion exchange mechanisms are the two major processes proposed for HAP as a divalent cation scavenger. For Pb^{2+} stabilization by HAP, the principal mechanism involved in the reaction is the dissolution of HAP followed by the precipitation of pyromorphite $[\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2]$ that is one of the most stable forms of lead compounds in the environment. The mechanism follows reactions (1) and (2) respectively:



5. 主な発表論文等

〔雑誌論文〕 計0件

〔学会発表〕 計3件（うち招待講演 0件 / うち国際学会 3件）

1. 発表者名 Mitali Nag, Amirhomayoun Saffarzadeh, Takeshi Nomichi, Takayuki Shimaoka, Hirofumi Nakayama
2. 発表標題 Assessment on the degree of Stabilization of Pb in MSWI Fly ash by Different Particle Sizes of Waste Fishbone Hydroxyapatite
3. 学会等名 10th China-Japan Joint Conference on Material Recycling and Waste Management, Beijing, China (国際学会)
4. 発表年 2019年

1. 発表者名 Amirhomayoun Saffarzadeh, Mitali Nag, Takeshi Nomichi, Takayuki Shimaoka, Hirofumi Nakayama, Teppei Komiya
2. 発表標題 A novel approach for stabilizing heavy metals in municipal solid waste incineration (MSWI) fly ash using waste fishbone hydroxyapatite (FB-HAP)
3. 学会等名 2nd Euro-Mediterranean Conference for Environmental Integration (EMCEI 2019), Sousse, Tunisia (国際学会)
4. 発表年 2019年

1. 発表者名 A. Saffarzadeh, M. Nag, T. Nomichi, T. Shimaoka
2. 発表標題 State-of-the-art Technology for the Stabilization of Pb in the Incineration Fly Ash Using Waste Fishbone Hydroxyapatite
3. 学会等名 4th International Conference on Recycling and Reuse, Istanbul, Turkey (国際学会)
4. 発表年 2018年

〔図書〕 計0件

〔産業財産権〕

〔その他〕

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6. 研究組織

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7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8. 本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関